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**AUG 29 1997**

**OFFICE OF  
RESEARCH AND DEVELOPMENT**

**MEMORANDUM**

**SUBJECT: Initial Perchlorate Report**

**FROM: Kenneth W. Brown, Director, TSC, CMB**  
**Environmental Sciences Division (ESD)**

**TO: Kevin Mayer, Superfund**  
**Region IX**

Kevin, as per our conversation, please find attached an interim report that provides information pertaining to our initial effort(s) in the analytical/sampling/monitoring aspects of perchlorate in the environment. As you will note, some recommendations are provided along with information pertaining to a perchlorate work shop.

In the next couple of weeks, I hope to provide you with more definitive comments and recommendations. Also, on August 25, 1997, we met with Syl Hersh and Bob Curial of the IT Corporation. Both Bob and Syl are chemists and provided some informative information. They are interested in receiving copies of this and other correspondence that the TSC provides to the Region.

Please let me know if I may send Bob and Syl copies of the attached report. I will be out of the office from August 29th through September 7th, 1997. If you need additional clarification and/or information pertaining to the attached, please call Marion Edison at (702) 798-2202.

**Attachment**

**cc: Steve Pia, ECB**  
**Wayne Sovocool, ECB**

**Interim Technical Report  
Review of Methodology for the  
Analysis of Perchlorate in Water**

Superfund Technical Support Product  
in support of EPA Region 9  
San Francisco, CA

J. R. Donnelly  
Lockheed Martin Environmental Services

Report Prepared for:  
U.S. Environmental Protection Agency  
Technology Support Center for  
Monitoring and Site Characterization  
National Exposure Research Laboratory  
Environmental Sciences Division  
Las Vegas, Nevada 89193-3478

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## **I. INTRODUCTION**

The Region 9 Superfund site Cleanup Branch Chief requested that the EPA-Las Vegas Technical Support Center critically review the California Department of Health Services (DHS) analytical protocol for the detection of perchlorate to the stated 4 ppb detection limit. This ion chromatographic (IC) method has been used to detect perchlorate in groundwater and surface water supplies in California, Arizona, and Nevada. It is considered important to establish the reliability of this method to detect perchlorate to the 4 estimated detection limit in support of the California level of concern that is set at 18 ppb. Additionally, effects of high dissolved solids should be addressed because of the presence of high dissolved solids typically present in groundwater and surface water in the arid southwest.

## **II. PROBLEM AND APPROACH**

The presence of perchlorate anion in water systems is associated primarily with the production and use of ammonium perchlorate, a rocket motor oxidizer. Because this chemical is used in only a few locations, little environmental research has been performed or widely disseminated on this chemical and the fate of the perchlorate anion in the environment or in biological systems.

The California DHS method was provided, but no method performance study results were included. The capabilities of the method should be defined, with respect to the following: false positives, false negatives, intra-laboratory and inter-laboratory precision and accuracy, sample holding times, sample preservation, and matrix effects such as dissolved solids/conductivity.

To address the request from Region 9, a search of the chemical literature was initiated using the chemical substance index of Chemical Abstracts. Perchlorate, sodium perchlorate, and potassium perchlorate were searched. The reason for searching the latter two salts is a combination of the fact that these cations are present in relatively high concentrations in water systems, and that sodium and potassium perchlorate salts have been subjected to considerable research having potential relevance. Once the ammonium perchlorate enters the water system, the ammonium cation usually becomes insignificant. Ammonium perchlorate research has primarily concerned the thermal stability and oxidizing properties of the solid salt.

## **III. PRELIMINARY FINDINGS**

The literature search is underway. Relevant publications from 1990 to present have been located. Several research type

analytical methods were found in the scientific literature. Ion chromatography (IC), such as that used in the DHS method, has been employed for inorganic anions including perchlorate. Therefore, the basic technology used in the DHS method is reasonable. Most research methods have utilized ppm concentrations, and the DHS reported 4 ppb detection limit appears to be uncommonly low.

The potential for false positives and false negatives should be studied. Research endeavors have provided outlines for such investigations using capillary electrophoresis (CE) and IC separations with a variety of detection systems including ion spray and electrospray mass spectrometry, conductivity, and Raman spectroscopy. Complementary analysis by one of these techniques would address and resolve interference issues regarding the reliability of the DHS IC method.

Little was found to date on sample holding times and preservation. Some data are available on chlorite and chlorate. The latter is reportedly stable for 18 days without a preservative. Reportedly, perchlorate formation and decomposition are unfavorable kinetically in such chemical systems, so the target anion may be more stable than chlorate.

The thermodynamics of perchlorate decomposition are favorable. Thus, it is potentially a powerful oxidizer. The kinetics are slow at ambient temperatures and in the absence of catalysis. Whether biological systems provide biochemical catalysts has not been found to date in the literature search. This question is key to answering concerns about the relative toxicity of the perchlorate anion in drinking water.

Limited data for one sample set were available from two laboratories. The results for low concentration samples (6 to 47 ppb) often varied up to about a factor of two between the laboratories. Higher level (440 to 1620 ppb) sample reported concentrations varied less than 20%. One laboratory reported results consistently higher than the other laboratory, suggesting that a difference may exist in actual vs. nominal concentrations of the perchlorate standards at one or both laboratories. Overall, the analytical differences are reasonable for low and high concentration interlaboratory results. Sample conductivities were measured to be 955 to 6780  $\mu\text{S}/\text{cm}$ . Conductivity was apparently not a factor in interlaboratory data variability. One laboratory reported testing the DHS method up to 7000  $\mu\text{S}/\text{cm}$ , with satisfactory results.

#### **IV. PLANNED FURTHER STUDIES**

Additional research findings will be sought through searching the chemical literature prior to 1990. It is now

believed that the bulk of relevant work on perchlorates probably will be found in the 1970 to 1990 time period, excepting the application of recently-developed analytical technologies such as electrospray mass spectrometry and capillary electrophoresis. One goal is to find data about the stability of perchlorate in the environment, particularly aqueous ecosystems. Additional information is also sought regarding toxicity studies in various biological systems, sample stability and holding times, potential interferences for IC and other methods, and reasonably achievable detection limits.

Certain laboratory-based studies are recommended, pending further research results that may be present already in earlier literature:

detection limit validation in aqueous matrices  
verification of method performance with high dissolved solids  
method precision, intra- and inter-laboratory  
method accuracy vs. confirmatory analysis results  
sample stability and preservation study vs. holding times

## **MARK SILVERSTEIN'S CONTRIBUTION**

August 27, 1997

## **Status on Information Gathering with Respect to Perchlorate in the Environment**

The three issues investigated are discussed below: (1) the most appropriate method(s) for collecting samples to be analyzed for perchlorate in water, (2) the fate and transport mechanisms by which perchlorate moves through the environment (i.e., via the soil and surface water and groundwater), and (3) potentially viable methods for remediating perchlorate in the environment.

These issues were initially investigated by contacting Lockheed Martin and other professionals working on perchlorate contamination issues and by accessing search engines on the Internet. The status of the information collection process is discussed below by major issue, and includes recommendations for further actions, where appropriate. In addition, based on this investigation, it was discovered that a workshop on perchlorate in groundwater is being organized. Details on this workshop are provided at the end of this report.

Information acquired with respect to the laboratory analysis of perchlorate and quality of such data is discussed in a separate attachment.

### **Perchlorate Sample Collection**

The only information acquired on collecting water samples for perchlorate analysis are those already recommended by (and is a standard protocol of) the California Department of Health Services (DHS). This method is not unlike water sample collection for the analysis of commonly measured anions (e.g., chloride, nitrate) in environmental samples.

Regardless of whether a surface water grab sample or a groundwater well sample from a pump or bailer is used, the sample can be collected in standard plastic or glass 250- or 500-mL sample bottles. Evidently, for ion chromatographic (IC) analyses, only a few mL of sample are needed, so the size of the bottle seems to be more a function of what the laboratory has a capacity to store in archive and/or must dispose of after analysis, rather than any volume requirement for analysis. While no preservative is added, the samples are typically shipped on ice (4 °C) to the laboratory. The maximum holding time for analysis has been set at 28 days, but it is not clear at this time if this limit is based on possible analyte degradation concerns or has been set simply to ensure a reasonable turnaround time for the analytical data. In addition, because of perchlorate's high degree of solubility in water (see below), there is apparently no concern of the chemical adhering to sampling equipment or sample bottles.

The above sample collection method is currently being employed at the site characterization effort at the former Lockheed Propulsion Company site in Redlands, CA, and presumably at other sites where sampling for perchlorate is being conducted.

## Perchlorate in the Environment

Ammonium perchlorate is very soluble in water (~20 parts per 100). Anecdotal information on the movement of perchlorate in water is that it acts like a "tracer." In effect, this means that the perchlorate ion essentially moves with the flow of the water and in the same hydrologic and hydrogeologic manner. Exceptions to this may include conditions when a concentrated "slug" of perchlorate enters the water system. The chemical may then disperse at a faster rate than the water through both the soil and the water system. Conversely, when conditions exist where the perchlorate is in more dilute or less concentrated levels than in the surrounding water system, it may diffuse more slowly. Over time, both of the above conditions will equilibrate to the point that the perchlorate will again flow evenly through the water system like a tracer.

## Remediation Possibilities

Based on the Internet search, a remediation technology was identified, which was demonstrated in 1995 at Tyndall Air Force Base, Florida. Mr. Stan Rising [(904) 283-6243; stan.rising@ccmail.af.mil], a chemical engineer involved in the demonstration of this technology was contacted. Wastewater from an ammonium perchlorate (AP) recapture process of Minuteman rocket propellant is processed through a bioreactor containing *Wolinella succinogenes* (a.k.a., HAP-1 organism), an anaerobic bacterium which "...can reduce AP to a nontoxic chloride product." According to Mr. Rising, the wastewater must contain the hundreds to thousands of parts per million (ppm) of perchlorate in order to satisfy the "nutritional" needs of the bacteria colony. The process has been shown to reduce perchlorate in the aqueous solution to non-detectable (i.e., parts per billion; ppb) levels. Thus, it is questionable whether this technology would be appropriate in the Las Vegas Wash/Lake Mead system based on the preliminary contamination levels measured. However, if such a technology was to be applied to this perchlorate contamination problem, a "pump-and-treat" process would seem appropriate.

(NOTE: Basic "off-the-shelf" ion chromatographic methods were used to analyze the wastewater samples for perchlorate at Tyndall AFB; thus, Mr. Rising could shed no light on possible alternative analytical methods.)

Mr. Rising mentioned work being performed at Lawrence Livermore Laboratory by Dr. Jeffrey Richardson (510-423-5187). According to Mr. Rising, Dr. Richardson is researching a method for removing lower levels of perchlorate than the HAP-1 process can handle, using a substance called "aerogel." Apparently this work is being supported by Aerojet. Dr. Richardson will not be available to confirm and expound upon this project until after this report has been submitted. Efforts at contacting Dr. Richardson will continue.

Mr. Rising also suggested that it may be feasible to remediate low-ppm levels of perchlorate from an aqueous matrix by exposing it to heated iron (or heating it and exposing it to iron). While there has been no work in this area to date, the process may be worth exploring.

## **Upcoming Workshop on Perchlorate in Groundwater**

Mr. Rising mentioned that Mr. Frank Blaha of the American Well Water Association (AWWA), Denver, CO, is in the process of organizing a meeting on perchlorate in groundwater. Contact was made with Mr. Blaha, who said that the invitee list for this workshop is currently in preparation.

While Mr. Blaha could not give the final details on the exact location of the workshop, he said it will take place in Ontario, CA on September 30 to October 2, 1997. There will be four main topics addressed at this workshop with respect to perchlorate:

- Analytical Methods
- Toxicology
- Treatment/Remediation
- Occurrence (i.e., where it is likely to be found)

Apparently a main proponent of this workshop has been the East Valley Water District, whose customers are constituents of Rep. Jerry Lewis (Riverside/Redlands, CA). The Southern Nevada Water Authority is also co-sponsoring this workshop by providing approximately 20% of the funding. He anticipates that Mr. Bruce Mackler (US EPA Region 9) will attend this workshop, as well as various experts in the above topics and representatives of environmental watchdog groups. Mr. Blaha also expects representatives of Aerojet will attend this workshop, and among other issues, will discuss advances in treatment systems.

Mr. Blaha also mentioned that there is currently a peer review of the DHS analytical method being conducted by Maj. Dan Rogers, Wright-Patterson AFB. The Air Force is also in the process of awarding a contract that addresses toxicological issues of perchlorate, where a two-generation study on the health effects of perchlorate in rats will be performed; a preliminary draft report is expected July 1998 which will recommend acceptable perchlorate doses in drinking water.

Mr. Blaha can be reached at 303-347-6244 and his supervisor, Ms. Debbie Brink, at 303-347-6109. Their fax number is 303-730-0851.